Comparative study of polar perovskite surfaces

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Abstract

A novel model of the "zig–zag" $(1\,1\,0)$ polar surface termination of ABO_3 perovskites is suggested and analyzed. Classical shell model calculations for $BaTiO_3$, $SrTiO_3$ and $LaMnO_3$ show that such the (1×2) $(1\,1\,0)$ surface reconstruction has the lowest energy, comparable to that for the $(1\,0\,0)$ surfaces. The calculated surface energy reaches the saturation only when 6–8 atomic near-surface planes are allowed to relax. Surface relaxation leads to the formation of considerable dipole moment perpendicular to the surface. The predicted surface polarization of thin perovskite films, even in the cubic phase, could affect their dielectric properties.
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1. Introduction

Thin films of ABO_3 perovskite ferroelectrics are important for many technological applications, including catalysis, microelectronics, substrates for growth of high T_c superconductors, where surface structure and its quality are of primary importance [1–3]. Several ab initio quantum mechanical [4–7] and classical Shell Model (SM) [8–11] theoretical studies were published recently for the $(1\,0\,0)$ surface of $BaTiO_3$ and $SrTiO_3$ crystals (hereafter BTO and STO). We are familiar with any surface cal-

culations for $LaMnO_3$ (LMO) which of great interest as the cathode material for fuel cells and due to colossal magnetoresistance. In order to study dependence of the surface relaxation properties on exchange-correlation functionals and localized/plane wave basis sets used in calculations, we performed recently a detailed comparative study based on a number of different quantum mechanical techniques [12–14]. The main conclusion was drawn there that the Hartree–Fock (HF), density functional theory (DFT), and even SM calculations give quite similar results for the atomic structure relaxation and surface energies.

The STO $(1\,1\,0)$ perovskite surface recently was studied experimentally using several different techniques; metastable impact electron spectroscopy

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gives a direct support to the formation of TiO on the faceted TiO$_2$ rows upon heating, atomic force microscopy also supports surface modification due to applied extensive thermal treatment [15–17]. However, we are familiar with no experimental estimates of the surface relaxation for the ABO$_3$ polar (1 1 0) surfaces, which could be compared with calculations. To our knowledge, only a few semi-empirical quantum mechanical calculations [18–20] exist so far for the (1 1 0) perovskite surfaces. We performed recently SM calculations of the atomic relaxation for the polar (1 1 0) surfaces of STO, BTO [11] and KNbO$_3$ [21]. In this short paper, we present a novel, "zig–zag" model for the polar (1 1 0) surface termination, and discuss results of the SM calculations for the relaxed atomic structure of the STO, BTO and LMO (1 1 0) surfaces.

2. Methods and surface models

We restrict ourselves to simulations of ABO$_3$ perovskites in the cubic crystalline phase, stable at high temperatures. Description of SM and its parameterization is available in Ref. [11]. Use of this model permits us to find the atomic relaxation for several hundreds of atoms, surface energies, along with the surface polarization, characterized by dipole moments perpendicular and parallel to the surface. This information is of great importance for analysis of dielectric properties of thin ferroelectric films. We allow atoms in a given number of near-surface planes (varied from 2 to 16) to relax to the minimum of total energy, and then analyze, how the major properties are affected by a number of relaxed planes. This is important since in time-consuming ab initio calculations only 2–3 near-surface planes are typically allowed to relax.

The well-known problem of modelling the (1 1 0) polar surface arises from the fact that it consists of charged planes. This is why, if the (1 1 0) surface were to be modelled exactly as one would expect after crystal cleavage, it would have an *infinite* dipole moment perpendicular to the surface, which makes such the surface unstable [3,22]. To avoid this problem, in our calculations we removed half the O atoms from the O-terminated surface, the Sr(Ba) atoms from the Ti-terminated surface, and

both the Ti and O atoms from the Sr(Ba)-terminated surface. As a result, we obtain the surface with charged planes but a zero dipole moment (before atomic relaxation). The relevant surface cells are built from neutral five-atom elements from three successive planes (see more in Ref. [11]). It should be noted here that, in principle, the polar surface could be stabilized due to the charge transfer between near-surface planes [3]. However, CNDO calculations [18] have shown that the surface energy of such the STO (1 1 0) exceeds by a factor of two the surface energies of the above-mentioned terminations with removed atoms.

The initial atomic configuration for the O-terminated surface, where every second surface O atom is removed and others occupy the same sites as in the bulk structure, we call asymmetric (A). Since such a removal of half of O atoms disturb the balance of interatomic forces along the surface, we also studied another, symmetric initial surface configuration (B) in which the O$_2$ atom is placed in the *middle* of the distance between two equivalent O atoms in the bulk. The A-type surface reveals considerable atomic displacements not only perpendicular to the surface, but also parallel to the surface. Preliminary results for the A-, B-cases were discussed in Ref. [11]. We study here one more configuration (C) which corresponds to the (1 × 2) surface reconstruction where O atoms are removed in a "zig–zag" way in nearest surface cells so that the remaining O atoms are alternating in the nearest cells on the left and right side from the B atom. In this case, there is no artificial dipole moment parallel to the surface, in contrast to the case A.

We analyzed recently [13,14] atomic displacements in the (1 0 0) outermost SrTiO$_3$ planes, obtained by means of various ab initio methods. In all calculations of the (1 0 0) surface energy, that for the SrO termination is only slightly smaller than for the TiO$_2$ termination. Thus, both (1 0 0) surfaces can co-exist, in agreement with the experimental observation [13].

3. Main results

Atomic relaxation of the first three top layers for BTO and STO was discussed in Ref. [11]. In

particular, we calculated there the relative displacement of O and Ti atoms in opposite directions from the top plane called *rumpling*. Our calculations predicted a large ≈14.5% (12.4%) a_0 rumpling for the TiO-terminated STO (BTO) surface. Atomic displacements in the third plane are still considerable, unlike the (1 0 0) surface. For the Sr(Ba)-termination, top Sr(Ba) atoms are displaced inwards, by ≈19% (13.5%), whereas the O atoms in the second plane go outwards, by ≈3.2% (2.8%).

The top O atom on the O-terminated asymmetric surface (A) of STO (BTO) is strongly displaced inwards, by ≈14.2% (11.2%), whereas the Ti atom in the second plane is also displaced inwards, but only by ≈2.4% (1.8%). Along with the displacements along the z axis perpendicular to the surface, all atoms here reveal also considerable displacements parallel to the surface. This results in the dipole moments p_y, to be discussed below. In contrast, for the symmetric termination B, atoms are displaced only along the z axis and reveal much smaller displacements (e.g., the top O atoms go inwards, by ≈3%.) However, Sr(Ba) atoms in the *second* plane are strongly (≈30.3% for Sr in STO and ≈26.5% for Sr in STO) displaced outwards the surface. Similar effect was observed by us for the $KNbO_3$ (1 1 0) surface [21].

Table 1 gives the results for the novel C-termination where atoms in alternating TiO_2 vertical planes move in opposite directions along the y axis. Overall, displacements of atoms in the top layers on the C-type surface are large and similar to those on the A-type surfaces, except for the Sr(Ba) and O ions in the second layer. These ions move only outwards, but due to the symmetry reasons their displacements along the y axis are

zero. To our knowledge, there are no low-temperature experimental data for the (1 1 0) surface— unlike the (1 0 0)—on the surface rumpling and compression/expansion of the top planes.

The macroscopic (1 1 0) *surface polarization* is characterized by the relaxation-induced dipole moments (per surface unit cells) p_z and p_y perpendicular and parallel to the surface, respectively. For the asymmetric termination (A) the surface polarization p_z oscillates, in both BTO and STO, around 1.1 eÅ with an increase of a number of relaxed near- surface planes (varied between 2 and 16). This is accompanied by a considerable dipole moment p_y parallel to the surface. In contrast, the p_z dipole moment for the B-type termination rapidly saturates (in BTO at 0.99 eÅ and in STO at 1.12 eÅ), whereas p_y rapidly goes to zero, with an increase of a number of relaxed layers. Lastly, for the "zig–zag" termination C, p_z oscillates around 1.1 eÅ in both BTO and STO, similarly to the asymmetric case (A) but without any dipole moment parallel to the surface. For the LMO (Fig. 1) A-termination, p_z oscillates around 1 eÅ similarly to the BTO and STO, being accompanied by large $p_y = 3.3$ eÅ. For the C-termination p_y vanishes and p_z is close to that for the A-termination.

In other words, surface relaxation of cubic perovskite structure leads to the considerable polarization perpendicular to the surface which results from near-surface relaxation. This could considerably affect the dielectric properties of thin films. Note that this effect is much less pronounced for the BTO (1 0 0) surface where $p_z = 0.07$ eÅ for BaO termination, and −0.19 eÅ for TiO_2 termination. (In STO, $p_2 = -0.045$ eÅ for SrO termination, and −0.12 eÅ for TiO_2 termination.)

Table 1
Atomic relaxation of three top layers (in percent of the lattice constant, a_0) of three ABO_3 perovskites for the C-type O- termination

Layer	Atom	STO		BTO		LMO	
		δ_z	δ_y	δ_z	δ_y	δ_z	δ_y
1	O	−13.76	±9.08	−9.93	±6.18	−6.88	±8.61
2	B	−4.87	±5.52	−3.01	±5.87	−2.13	±5.26
2	A	4.31	0.0	5.45	0.0	4.29	0.0
2	O	1.21	0.0	−0.93	0.0	1.27	0.0
3	O	−9.60	±7.54	7.98	±5.30	9.89	±4.08

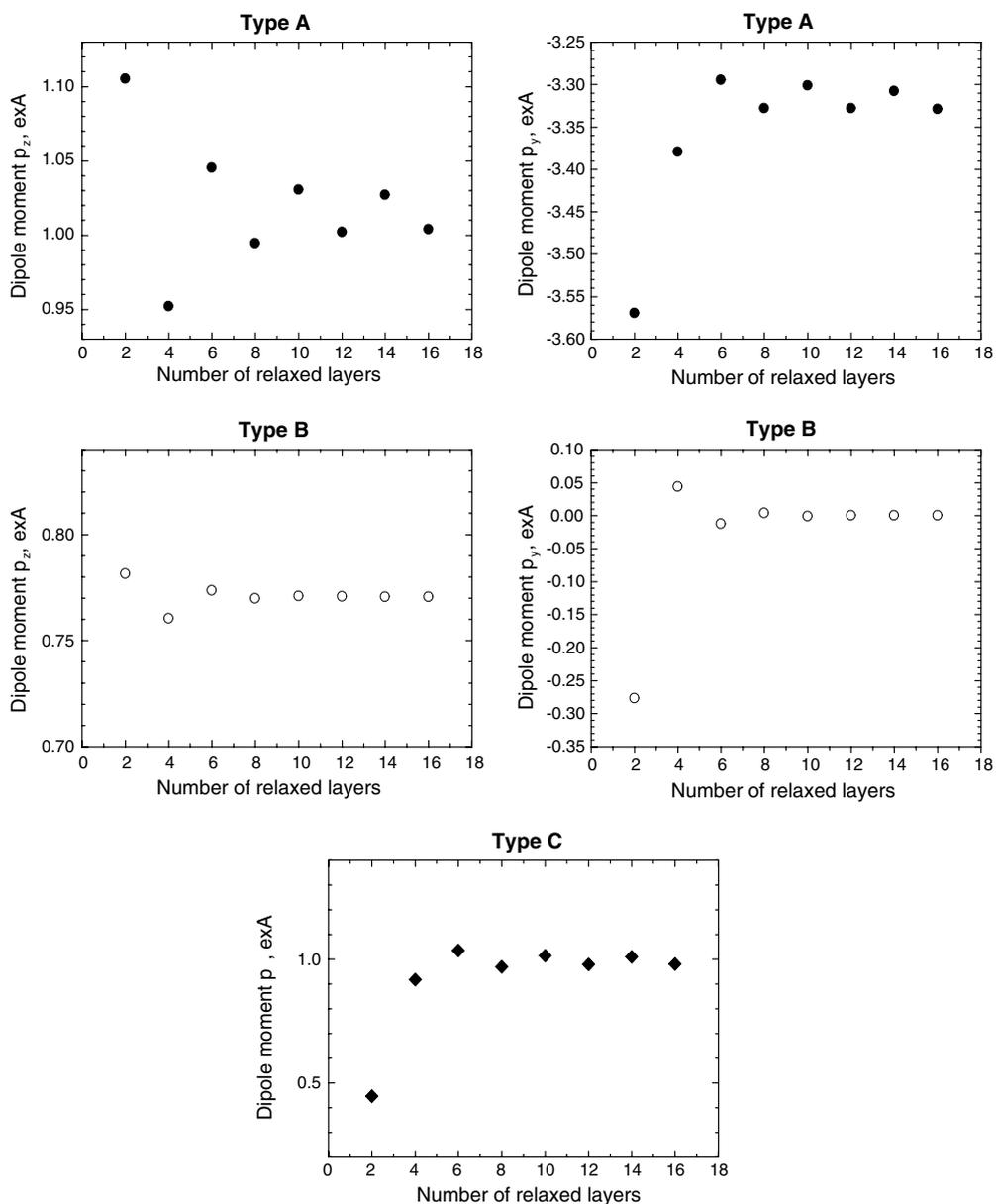Results for previous calculations of the A, B, TiO and Sr- terminations see in Ref. [11].

Polarization of O-terminated LaMnO$_3$ (110) Surface

Fig. 1. Surface polarization and dipole moments perpendicular and parallel to the LMO (1 1 0) surface with three different terminations.

Table 2 demonstrates a considerable difference for surface energies, obtained for two and 16 relaxed layers. Our calculations show that the (1 1 0) surface energy saturates only at about 6–8 relaxed layers, whereas in ab initio calculations only 1–2

layers are typically relaxed. Unlike the (1 0 0) surface, different (1 1 0) surface terminations strongly differ in energies. For all three perovskites, the novel, "zig–zag" termination C reveals the lowest surface energy. For the BTO and STO this is close

Table 2
Surface energies for four different O (1 1 0) terminations as calculated for STO, BTO and LMO perovskites

Type	SM-2	SM-16
STO A-type	1.54	0.92
B	3.13	3.31
C	1.63	0.76
TiO	2.21	2.36
Sr	3.04	3.37
BTO A-type	1.58	1.83
B	4.66	4.84
C	1.84	1.82
TiO	2.11	2.36
Ba	3.79	4.16
LMO A-type	2.59	2.06
B	4.11	4.06
C	2.80	1.95

SM-2, SM-16 refer to the number of near-surface planes allowed to relax.

to the (1 0 0) surface energy. In contrast, the surface energies for the LMO are considerably larger than the relevant energies for the BTO and STO.

4. Conclusions

We would like to stress that the lowest surface energy for all three perovskites is predicted for the novel "zig–zag" (1×2) reconstructed surface termination. This reveals no dipole moment parallel to the surface, but a considerable dipole moment perpendicular to the surface, which certainly can affect the dielectric properties of thin perovskite films.

Acknowledgements

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